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Nanoindentation Technique at Investigating of Aluminum Oxide - CrC Nanoparticles Composite Coating

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ABSTRACT

In this paper fatigue and fracture of Al-Al₂O₃-CrC nanostructured composite coatings was investigated by nanoindentation technique and in-situ experiments performed by a scanning electron microscope to permit examination of freshly exposed surfaces. Crystallographic and morphological textures were characterized and fracture resistance was measured. CrC layer improves fracture resistance of alumina layer. CrC layer produced by pyrolytic deposition (CVD) may effectively heal pores and defects of alumina layer. It resulted in high load rating of the composite coating. Experiments reveal that in all cases, the detection of an acoustic signal corresponded to the appearance of a circular cracks seen on surface; in a very few cases, examination of surface after detection of a signal revealed presence of two ring cracks. Degree of toughening associated with crack healing is determined by a number of healed defects and an effectiveness of an individual healing.

INTRODUCTION

Aluminum oxide-based nanocomposites are useful as structural elements of micro machines and devices because of its high hardness and load rating, low wear rate, high stiffness-to-weight ratio, and high-temperature stability, but suffer from low fracture resistance. When aluminum oxide layers are formed by micro arc oxidizing, extremely high adhesion (350-400 MPa) to aluminum substrates are achievable [1]. Enhanced hardness has been reported for aluminum oxide matrixes containing alpha and gamma phases of aluminum oxide, both for single-crystal superlattices inspected [2] as well as for polycrystalline nanostructured multilayers studied by Chu et al. [3].

In polycrystalline aluminum oxide matrix, high hardness is explained by the presence of dislocation between the nanostructured interfaces that are resulted from the difference in the shear module of the materials and coherency strains for small periodicity superlattices with significant lattice mismatch between the layers as shown by M. Shinn et al. [2].

Known technology of micro arc oxidizing uses high current densities (up to 40 A/dm²) when aluminum oxide grows up on aluminum substrate [4]. The current may induce large defects, micro voids and pores in formed aluminum oxide structure [5]; however, aluminum oxide layer consists of two principal phases: alpha and gamma [6]. This may result in its superior mechanical properties. Nevertheless, the structural mismatches do depreciate benefits of oxide aluminum structure while its application as wear protective coating or thermal barrier layer.

An objective of the paper was to investigate the possibility to improve physical and mechanical properties of aluminum oxide-based coating by CrC-based nanoparticles produced by a metal organic chemical vapor deposition (CVD). In the present paper, nanoindentation has been used to investigate fracture and fatigue of Al-Al₂O₃-CrC composite coatings. Indentation technique was used as a perfect tool for characterizing the performance and durability of the composite coating.

EXPERIMENTAL PROCEDURE

The combination of an AFM and a nanoindenter (for example, MicroSystems, UK) is a further development of the traditional Vickers microhardness testing device. This instrument allows for two measurement modes. It provides a surface topography of constant contact force in AFM mode and a force displacement curve in nanoindentation mode using the same tip. This feature provides a high spatial resolution to position the tip on the microstructure of interest. The sample is mounted on a scanner that allows for a movement in the plane normal to the axial motion of the tip. The transducer consists of a three-plate capacitor on whose central plate a tetrahedral diamond

Berkovich-tip is mounted. A nanoindentation curve plotted a loading phase where the tip is pressed into the material up to a maximal force, a holding period where the tip creeps into the material and an unloading phase where the force on the material is released. The loading and holding phases result in both plastic and elastic deformation that cannot be distinguished. The unloading phase shows the elastic recovery of the material while the load is released. The contact area A_h is determined by a procedure derived by Oliver et al.[7, 8].

The 5054 aluminum alloy as it's referred in the MIL specifications was substrate on which Al₂O₃ layer was produced by micro arc oxidizing. Al₂O₃ layer has up to 10 % pores on the outside of a sample. Pores diameter ranges between 0.5 and 4.5 μm . The thickness of the alumina layer was 250 μm , its microhardness was between 16 and 18 GPa and its Young's modulus was 290 GPa.

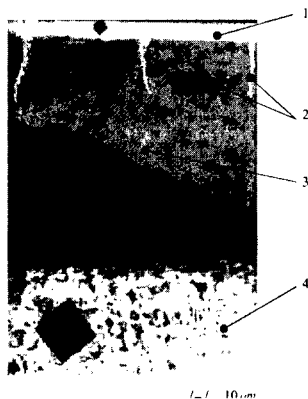


Figure 1. Al-Al₂O₃-CrC nanostructured composite coating

Pyrolysis technology or CVD may deposit CrC nanoparticles on aluminum oxide surfaces. Pyrolytic deposition was performed by a pyrolysis of a metal-organic liquid (Barhos) consisting of Cr-organic compounds under vacuum in pressure range between 4 and 8 Pa. Principal pieces of equipment are a vertical quartz tube reactor, a feeder of a liquid composed of Cr-organic compounds and two cylinder furnaces located inside an internal space of a reactor. Reactor is connected with a vacuum pump through an entrainment separator. Chromium-organic liquid is fed into an upper furnace and evaporates in its inner volume. Vapors of chromium-organic compounds are then delivered to aluminum oxide substrate placed on a special holder inside a lower furnace, where they decompose forming a coating. Temperature of aluminum oxide surface was between 430 and 450°C.

Produced Al-Al₂O₃-CrC composite coating have pores and defects of alumina layer filled by the CrC nanoparticles (see indexes on fig. 1). The nanoparticles form hard CrC layer having low residual strains. Thickness of CrC layer ranges from 10 to 50 µm, its microhardness was 17,5 GPa and its Young's modulus was 300 GPa.

Nanoindentation response of aluminum oxide-CrC nanoparticles multilayered composite coating and homogeneous aluminum oxide coating were determined using a NanoIndentory II instrument. The measurement procedure was as follows: load to maximum, unload to 10% of maximum load, hold for 50 s, load to maximum, hold for 200 s, and completely unload. The maximum load was 10 or 50 mN and a maximum of ten indents sequences were used for each maximum load. The data from the first hold segment ~50 s was used to correct the load-displacement data for thermal drift. The triangular Berkovich diamond indenter tip was calibrated following the procedure described in Ref. [7, 8].

RESULTS & DISCUSSION

The main topics for this section are (1) to explain hardness increase when additional CrC nanoparticles are introduced into the aluminum oxide layer creating aluminum oxide-CrC multilayered composite coating, as compared to few reported hardness enhancement for both a single aluminum oxide layer and may be polycrystalline nanostructured aluminum oxide composite, and (2) to discuss the fracture behavior of aluminum oxide-CrC composite coating. Before discussing these topics, however, I briefly address the phase structure and the residual stress state of the as-deposited CrC nanoparticles. In both cases, superstructure strengthening-hardening is explained based on dislocation glide across nanostructure limited by the shear modulus difference and dislocation glide within individual layers and/or multilayers.

Figure 1 shows that the CrC nanoparticles deposited on Al₂O₃-based layer fill its pores and other structural defects like cracks. CrC nanoparticles and whole CrC layer have high adhesion to aluminum oxide substrate since no exfoliation is visible in the fracture of the coated specimens at applied technological regimes. The composite coating is characterized by a fine-grained globule-like structure. It should be pointed out that one structure may consist of several grains, CrC nanoparticles or subgrains, therefore size of CrC nanoparticle is actually less than width of a pore.

X-ray analysis revealed that CrC top layer consists of generally chromium carbides (Cr₃C₂ and Cr₇C₃). CrC layer heals various surface defects, pores and voids on aluminum oxide surface (see fig. 1), which was deeply determined by studying a coating-substrate interface with an aid of SEM.

Electrochemical studies and SEM investigations revealed that aluminum oxide-CrC composite coating is very dense and virtually defect-free. The healing is resulted by CrC nanoparticles that fill the most defects of aluminum oxide structure. Single oxide aluminum layer was formed; however, the failure is initiated by "opening" defects of aluminum oxide structure. It results in a poor fracture resistance of an aluminum oxide against an initiation and propagation of micro and nanocracks through its defects and pores.

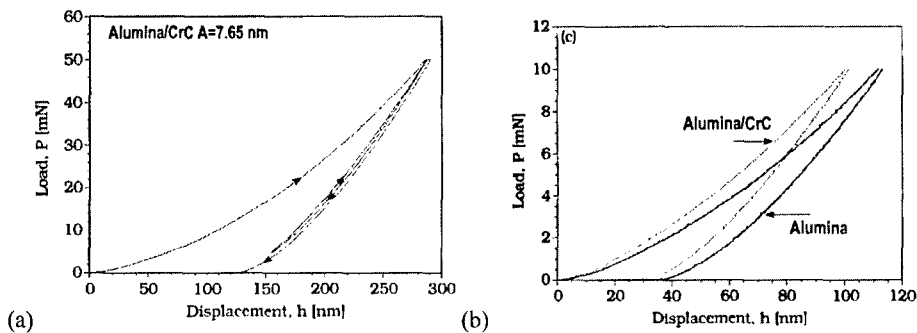


Figure 3. Nanoindentation curves

Figure 3a,b show nanoindentation load-displacement curves from aluminum oxide-CrC multilayered composite coating. A typical curve obtained with 50 mN maximum load is shown for the composite coating at Fig. 3a,b and for a single oxide aluminum structure at Fig. 3b.

The initial loading segment contains an elastic-plastic displacement. The first unloading curve and the second loading curve differ substantially and form a hysteresis loop with a larger displacement rather during unloading than loading. The data from the first hold segment was used for correction of the load-displacement data for thermal drift and the second for investigating creep like dislocation nucleation and glide plastic behavior. Approximately 5-8 nm maximum load creep occurred at the maximum load hold segment in Fig. 3.

Aluminum oxide-CrC-based nanostructured composite coating has the maximum displacement between 270 and 280 nm. It is less than that of single aluminum oxide layer. The first and the second unloading curves from the coatings show actually the same elastic behavior with a small creep. However, the elastic response from the coatings may differ and thus result in the different apparent hardness. Single aluminum oxide layer exhibited the largest percentage of elastic recovery from maximum displacement during the second unloading.

Hardnesses of the aluminum oxide layer was in the range of published nanoindentation hardness data between 16 and 26 GPa, depending on coating microstructure and hardness evaluation procedure. Hardnesses of aluminum oxide-CrC composite coating was in the range of data between 20 and 28 GPa, depending on coating microstructure, thickness of its layers and hardness evaluation procedure.

Higher standard deviations found in previous nanoindentation studies were probably associated with averaging over multiple samples. Despite of this, the results indicated that, in first approximation, the composite coating may be seen as a nanoassembly of CrC nanoparticles and aluminum oxide particles with distinct oxide and carbide phases between them, but rather homogeneous mechanical properties within the same nanostructured elements. This finding has

potentially important implications in the process of fracture propagation that is clearly related to composite coating structure and its heterogeneity.

Major limitation of nanoindentation data analysis remains the hypothesis of isotropy of tested material. In fact, the indentation curve depends to a widely unknown extent on all anisotropic elastic constants of the tested material. Since aluminum oxide-CrC nanostructured composite coating and most probably also single aluminum oxide layer are elastically anisotropic, the reported results are some weighted average of the elastic moduli along the various material orientations.

CONCLUSION

CrC nanoparticles and all CrC coating deposited with the aid of metall-organic CVD on aluminum oxide coating, which is composed of a mixture of Cr and chromium carbides, has good microhardness as high as 20 GPa, fracture resistance and an adhesion to the substrate. CrC layer may have very strong chemical and structural interaction with aluminum oxide substrate when depositing. CrC nanoparticles leads to healing various surface defects and pores of aluminum oxide layer and retardation of the crack initiation and its propagation in the near-surface.

Fracture of Al-Al₂O₃-CrC nanostructured composite coating have been investigated by nanoindentation in-situ experiments. CrC layer may effectively improve the fracture resistance of Al₂O₃ layers by healing defects of aluminum oxide structure such as its pores, internal voids, cracks etc. The degree of toughening associated with crack healing is determined by the number of healing defects and the effectiveness of the individual healing. It may result in enhanced strength, fracture toughness, and microhardness of coated aluminum oxide ceramic specimens.

In general, damage of Al-Al₂O₃-CrC composite coating is suppressed, in contrast to that of single Al-Al₂O₃ coating. Principally, the effect of healing results in high load rating of the Al-Al₂O₃-CrC composite coating, but the contact strains at loading may be higher then that of a single layer. CrC nanoparticles and clusters deflect corresponding to deformation plastic material flow. Deformation may take place in radial spreading of contact zone under indenter with initiation of local cracks.

Nanoindentation technique is powerful approach to investigate fracture mechanics of the coatings. It is expected that nanoindentation modeling for a contact of an indenter and a body would be effectively modified by rheological equations [9, 10]. Therefore, rheological analysis and principal Hertzian equations may be applied together to consider not only elastic and plastic properties of contacted materials, but also viscous properties of a sample and an indenter.

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